AFRL-ML-WP-TR-2004-4226

NONDESTRUCTIVE EVALUATION (NDE) TECHNOLOGY INITIATIVES PROGRAM (NTIP)

Delivery Order 0041: Advanced Processing of Novel Ni-Based Single Crystal Alloys

Tresa M. Pollock, Ph.D.

University of Michigan
Division of Research Development and Administration
3003 South State Street
Ann Arbor, MI 48109-1274

JANUARY 2004

Final Report for 01 October 2002 – 31 August 2003

Approved for public release; distribution is unlimited.

STINFO FINAL REPORT

MATERIALS AND MANUFACTURING DIRECTORATE
AIR FORCE RESEARCH LABORATORY
AIR FORCE MATERIEL COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7750

NOTICE

WHEN GOVERNMENT DRAWINGS, SPECIFICATIONS, OR OTHER DATA INCLUDED IN THIS DOCUMENT FOR ANY PURPOSE OTHER THAN GOVERNMENT-RELATED PROCUREMENT DOES NOT IN ANY WAY OBLIGATE THE US GOVERNMENT. THE FACT THAT THE GOVERNMENT FORMULATED OR SUPPLIED THE DRAWINGS, SPECIFICATIONS, OR OTHER DATA DOES NOT LICENSE THE HOLDER OR ANY OTHER PERSON OR CORPORATION, OR CONVEY ANY RIGHTS OR PERMISSION TO MANUFACTURE, USE, OR SELL ANY PATENTED INVENTION THAT MAY RELATE TO THEM.

THIS REPORT IS RELEASABLE TO THE NATIONAL TECHNICAL INFORMATION SERVICE (NTIS). AT NTIS, IT WILL BE AVAILABLE TO THE GENERAL PUBLIC, INCLUDING FOREIGN NATIONALS.

THIS TECHNICAL REPORT HAS BEEN REVIEWED AND IS APPROVED FOR PUBLICATION.

Patrick L. Martin

PATRICK L. MARTIN, Project Engineer
Metals Development Section
Metals, Ceramics & NDE Division

Rollie E. Dutton

ROLLIE E. DUTTON, Chief
Metals Branch
Metals, Ceramics & NDE Division

Gerald J. Petrak

GERALD J. PETRAK, Assistant Chief
Metals, Ceramics & NDE Division
Materials & Manufacturing Directorate

DO NOT RETURN COPIES OF THIS REPORT UNLESS CONTRACTUAL OBLIGATIONS OR NOTICE ON A SPECIFIC DOCUMENT REQUIRES ITS RETURN.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
January 2004	Final	10/01/2001 – 08/31/2003

4. TITLE AND SUBTITLE
NONDESTRUCTIVE EVALUATION (NDE) TECHNOLOGY INITIATIVES PROGRAM (NTIP)
Delivery Order 0041: Advanced Processing of Novel Ni-Based Single Crystal Alloys

5a. CONTRACT NUMBER
F33615-97-D-5271-0041

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
62102F

6. AUTHOR(S)
Tresa M. Pollock, Ph.D.

5d. PROJECT NUMBER
4349

5e. TASK NUMBER
40

5f. WORK UNIT NUMBER
01

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of Michigan
Division of Research Development and Administration
3003 South State Street
Ann Arbor, MI 48109-1274

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Materials and Manufacturing Directorate
Air Force Research Laboratory
Air Force Materiel Command
Wright-Patterson AFB, OH 45433-7750

10. SPONSORING/MONITORING AGENCY ACRONYM(S)
AFRL/MLLP

11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S)
AFRL-ML-WP-TR-2004-4226

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; release is unlimited.

13. SUPPLEMENTARY NOTES
Report contains color.

14. ABSTRACT
The overall objective of this program was to define new nickel-base superalloy single crystal compositions with improved properties compared to current commercial alloys. In addition to improved properties, these alloys would be amenable to processing by new single crystal liquid metal cooling processes. Alloys were subjected to a range of microstructural characterization, non-destructive evaluation and mechanical and physical property evaluations. Some compositions with improved properties relative to current "Generation 3" single crystal alloys were identified.

15. SUBJECT TERMS
Single crystals, superalloy, compositions

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT:	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON (Monitor)
a. REPORT	b. ABSTRACT	c. THIS PAGE			Pat Martin
Unclassified	Unclassified	Unclassified	SAR	16	19b. TELEPHONE NUMBER *(Include Area Code)* (937) 255-1353

Program Summary

The overall objective of this program was to define new nickel-base superalloy single crystal compositions with improved properties compared to current commercial alloys. In addition to improved properties, these alloys would be amenable to processing by new single crystal liquid metal cooling processes. Alloys were subjected to a range of microstructural characterization, non-destructive evaluation and mechanical and physical property evaluations. Some compositions with improved properties relative to current "Generation 3" single crystal alloys were identified.

Approach

The overall approach to improving the temperature capability of these single crystals was to utilize ruthenium additions. In our prior research, we have discovered that additions of Ru increase liquidus temperatures and permit controlled partitioning of elements (including Re) between the gamma and gamma prime phases, resulting in improved creep properties. Additionally, Ru additions permit fairly substantial additions of Cr, well beyond what is present in recent commercial alloys. This provides a significant benefit to oxidation properties, particularly at 1100˚C. In this program, further improvements in the high temperature capabilities of these Ru-containing single crystals were pursued.

Several promising compositions from our previous work with Alstom Power Inc. of Baden, Switzerland were utilized as the starting point for this investigation. These prior alloys were designated F16-F25 in Table I. The long-term phase stability (specifically the overall resistance to precipitation of detrimental TCP phases) was examined in alloys F16-F25 prior to selection of new alloys for this effort. Long-term exposures were conducted at 950˚C for 1500 h and samples were subsequently examined by scanning electron microscopy for the presence of any detrimental phases. Among these alloys, F20 displayed the best combination of creep properties and phase stability at 950˚C. The creep behavior at 950˚C and 290 MPa of selected Ru-containing experimental alloys, including F20, is shown in Figure 1. Considering possible improvements in F20, five additional alloys based on this composition were then formulated: F26-F30, Table 1. The selected additions were aimed at further improvements in high temperature strengthening. From preliminary investigations of the five alloys, three additional experimental alloys with higher amounts of refractory elements were cast: F31-F33, Table 2.

All alloys were solidified as single crystals in a unique furnace at the University of Michigan. This system has the capability for solidification in the conventional Bridgman mode or with use of liquid metal Sn-assisted cooling. The main chamber of the single crystal growth system is shown in Figure 1. The furnace is capable of casting 5 kg of Ni-base superalloy into 300 mm tall molds on a 150 mm diameter chill plate. Investment molds were fabricated by PCC Airfoils, Inc. Conventional "pigtail" type starters were used and bars were solidified in clusters with a maximum of 4 bars per mold. Investment molds were preheated to 1550˚C and withdrawn at a rate of 3.3 mm/min (8 in./h.).

Figure 1 – Chamber of the Bridgman/LMC-Sn system at the University of Michigan. The tin bath is supported by the outer door (to the left). Crucibles are top loaded into the 50kW induction coiled, melted and bottom poured into the the preheated investment mold.

Results

Long-term exposure of the F20 alloy at 950˚C revealed no precipitation of detrimental phases after 3000 hours, Figure 3. This is a promising result considering the high amount of Cr (8 at%) in the experimental alloy. Our prior work has shown that the class of alloys being investigated here typically have better cyclic oxidation properties than "Generation 2" alloys such as CMSX-4 and Rene'N5. The high level of phase stability was observed over a range of temperature, with no detrimental phases appearing after exposures at 800˚C for 1250 hours, Figure 4, or 1100°C for 1100 hours, Figure 5.

The new alloys, F26-F30, were melted with standard vacuum induction melting techniques at Sophisticated Alloys, Inc. The polycrystalline ingots were cast into single crystals bars in the UM facilty described above. The as-cast microstructures of the bars revealed that these alloys do solidify as single crystals with no composition-induced convective instabilities that result in defects such as freckles and misoriented grains. The primary dendrite arm spacings of the experimental alloys were approximately 300μm.

Differential thermal analysis of the experimental alloys was conducted to determine the liquidus and solidus temperatures of the new alloys, Table 3. All of the liquidus temperatures were within a few degrees of 1400˚C. Preliminary heat treatments revealed no detrimental phases in these alloys after solution treatments and aging at 100 hours at 1100°C.

Solution treatment of the single crystal alloys resulted in a volume fraction eutectic of less than 5% in all cases. The solution temperatures of the experimental alloys are given in Table 3. The solution temperature of F29 is significantly lower than the solution temperatures of the other experimental alloys; the volume fraction eutectic is also higher. Apparently the addition of 1at% Mo lowers the γ' solvus in this alloy. Mo additions produced a similar effect in the F24 alloy. An overview of the single crystal microstructures of the new alloys after solution treating and aging is given in Figure 6.

The solution treated and aged single crystal bars were machined into creep specimens by Westmoreland Mechanical Testing and Research Inc. for mechanical property evaluations. The experimental alloys F26, F27, F28 and F30 were crept for 200 hours at 950°C and 290 MPa. Their creep behavior at 950˚C and 290 MPa is shown in Figure 7, in addition to the creep curve for MK-4 (a current commercial superalloy which is a minor modification of CMSX-4). The experimental alloys are more resistant to creep deformation at these conditions and furthermore, are still in the steady state regime while the commercial superalloy has reached the tertiary creep regime during the 200 hour test.

One of the experimental alloys, F30, is significantly more resistant to creep deformation at 950°C and 290 MPa. The alloy UM-F30 has 10 at% Co compared to 2.5 at% Co in the other experimental alloys. From the single crystal microstructures, F30 appears to have smaller γ' precipitates than F26, F27 and F28. In the 200 hour creep test, F30 has strained 0.3%, while the next strongest alloy has strained 0.8%. Measurements of the

rupture life of this alloy are still in progress. Creep rupture tests at 950°C are complete for MK-4, F20 and F27, Figure 8. The creep rupture life of F27 is twice as long as F20 and more than three times longer than MK-4. In Figure 9 the results for the F20 and F27 alloys are plotted on a Larson-Miller plot for comparison to Rene'N5, Rene'N6 and CMSX-4. Note that F27 has slightly better properties than the third generation single crystal Rene'N6, even with a lower amount of Re+W, compared to Rene'N6. Based on the interrupted creep curve shown in Figure 7, it is expected that the Alloy F30 will be substantially more creep resistant than Rene'N6 and F27. Further work beyond the end of this program will characterize the creep behavior of all new alloys at 1100°C and continue creep rupture tests at 950˚C.

Table 1 - Compositions of Experimental Alloys (at%)
(Air Force alloys in red formulated based on F20)

Alloy	Ni	Al	Ru	Ta	Re	W	Co	Cr	Mo	Ti
UM-F16	59.15	14.3	6	2.25	1.3	1.5	7.5	8		
UM-F17	69.95	14.3	3.5	2.25	1.5	1	7.5			
UM-F18	69.95	13.8	3.5	2.75	1.5	1	7.5			
UM-F19	61.95	13.8	3.5	2.75	1.5	1	7.5	8		
UM-F20	66.95	**13.8**	**3.5**	**2.75**	**1.5**	**1**	**2.5**	**8**		
UM-F21	63.15	14.3	6	2.25	1.3	1.5	7.5	4		
UM-F22	70.95	13.8	3.5	2.75	1.5	1	2.5	4		
UM-F23	66.2	14.3	6	3.5	1.5	1	7.5			
UM-F24	65.2	14.3	6	3.5	1.5	1	7.5		1	
UM-F25	65.7	13.8	6	3.5	1.5	1	7.5	8		1
UM-F26	66.35	13.8	3.5	2.75	1.5	**1.5**	2.5	8		
UM-F27	65.95	13.8	3.5	2.75	**2.5**	1	2.5	8		
UM-F28	66.45	13.8	3.5	**2.5**	1.5	1	2.5	8		**0.5**
UM-F29	65.95	13.8	3.5	2.75	1.5	1	2.5	8	**1**	
UM-F30	58.95	13.8	3.5	2.75	1.5	1	**10.5**	8		

Table 2 - Compositions of Experimental Alloys (at%)
Higher Refractory Alloys

Alloy	Ni	Al	Ru	Ta	Re	W	Co	Cr	Ti
F31	65.45	13.8	3.5	2.75	2.5	1.5	2.5	8	
F32	57.45	13.8	3.5	2.75	2.5	1.5	10.5	8	
F33	65.2	13.8	3.5	2.5	2.5	1.5	2.5	8	0.5

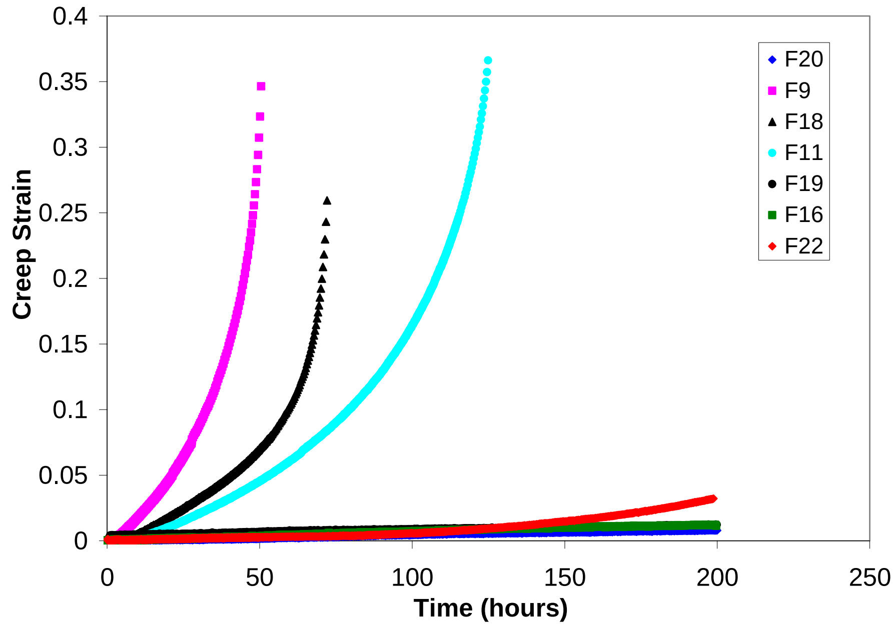


Figure 2 – Creep Behavior of Prior Experimental Alloys

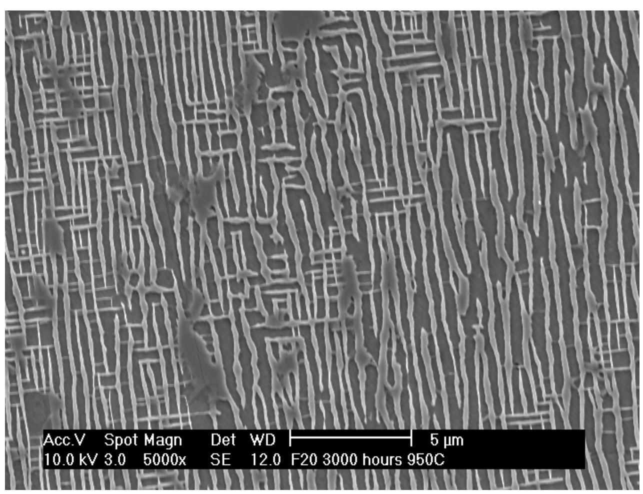


Figure 3 – Microstructure of UM-F20 after 3000 hours at 950°C

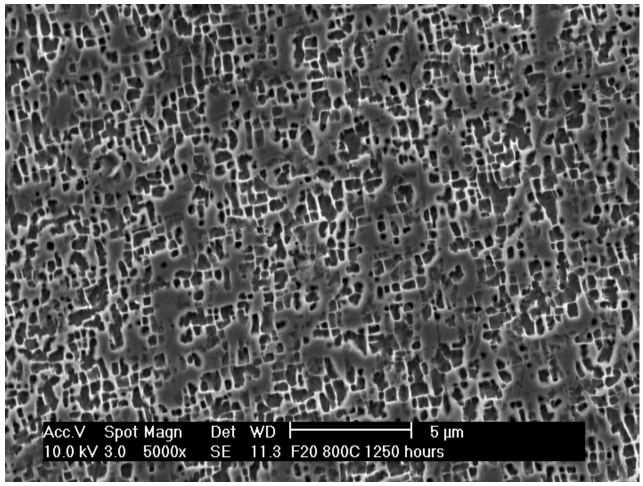


Figure 4 – Microstructure of UM-F20 after 1250 hours at 800°C

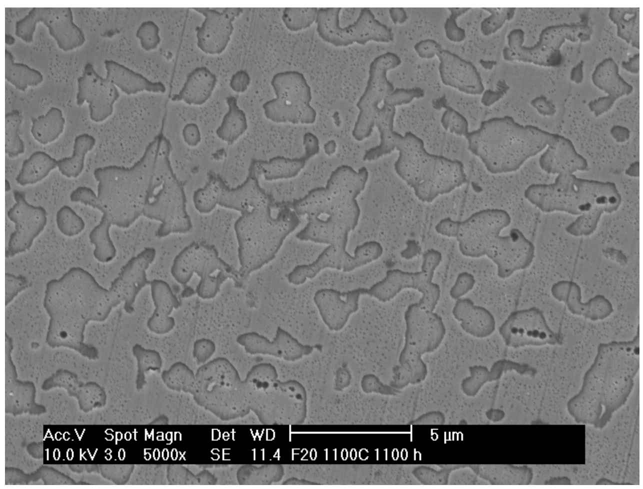
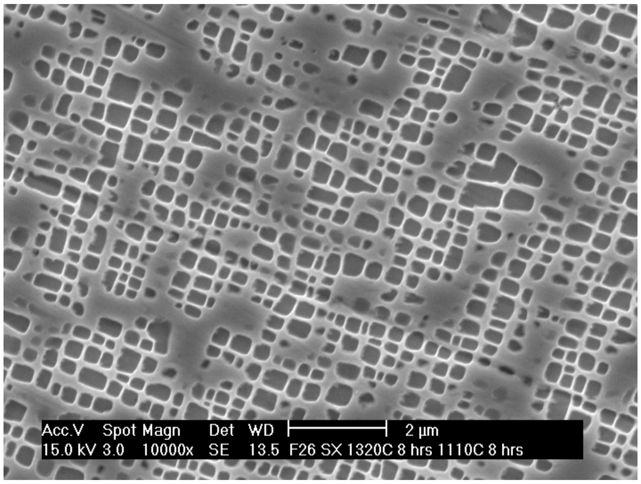


Figure 5 – Microstructure of UM-F20 after 1100 hours at 1100°C

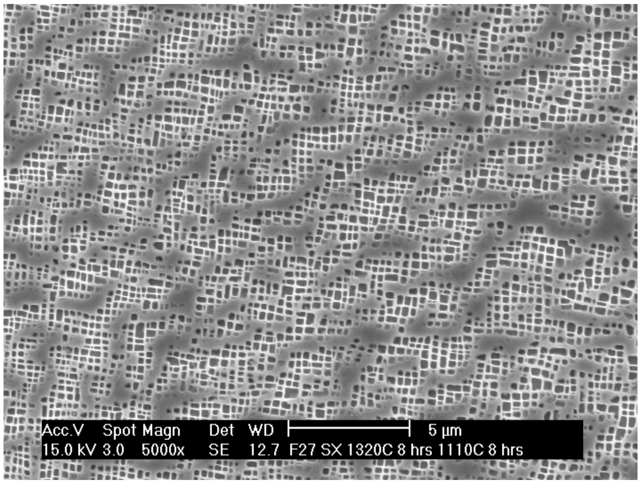
Table 3 – As-Cast Volume Fraction Eutectic and Results of DTA Analyses

Alloy	Volume Fraction Eutectic	Solution Temp.	Liquidus Temp.	Solidus Temp.
F20	15%	1300°C	1400°C	1366°C
F26	10%	1320°C	1398°C	1359°C
F27	10%	1300°C	1404°C	1358°C
F28	13%	1320°C	1397°C	1357°C
F29	19%	1250°C	1387°C	1338°C
F30	6%	1290°C	1398°C	1358°C

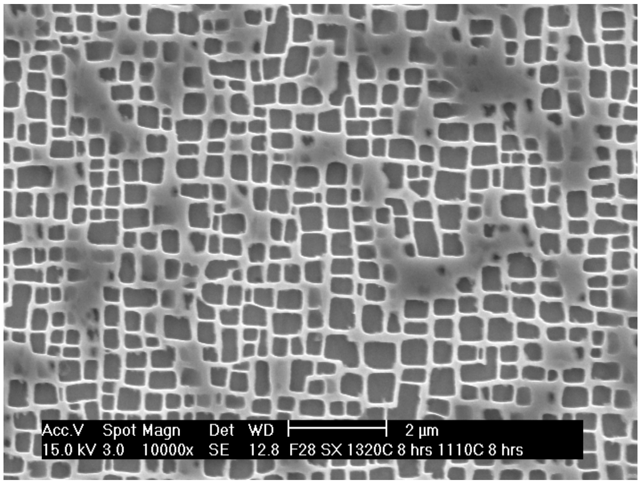
UM-F26 Single Crystal Microstructure - 1320ºC 8 hours +1100ºC 8 hours



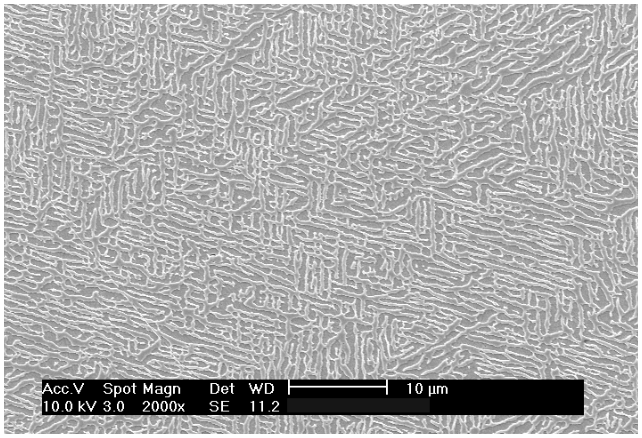
UM-F27 Single Crystal Microstructure - 1320ºC 8 hours +1100ºC 8 hours



F28 Single Crystal Microstructure - 1300ºC 4 hours +1100ºC 100 hours



F29 Polycrystalline Microstructure - 1280ºC 4 hours +1100ºC 100 hours



F30 Single Crystal Microstructure - 1320ºC 8 hours +1100ºC 8 hours

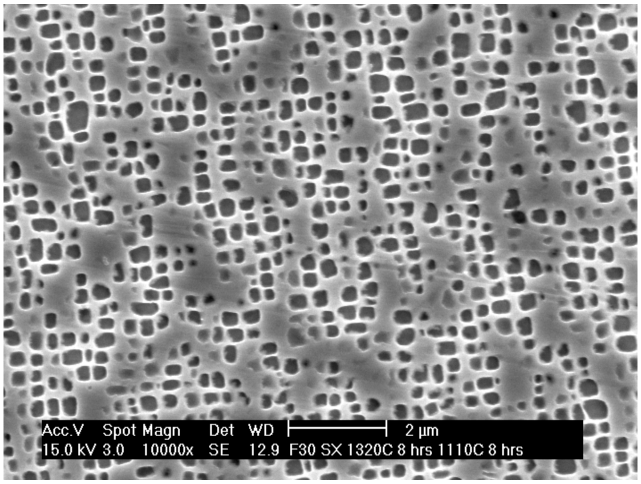


Figure 6 - SEM Images of the Microstructures of the Experimental Alloys

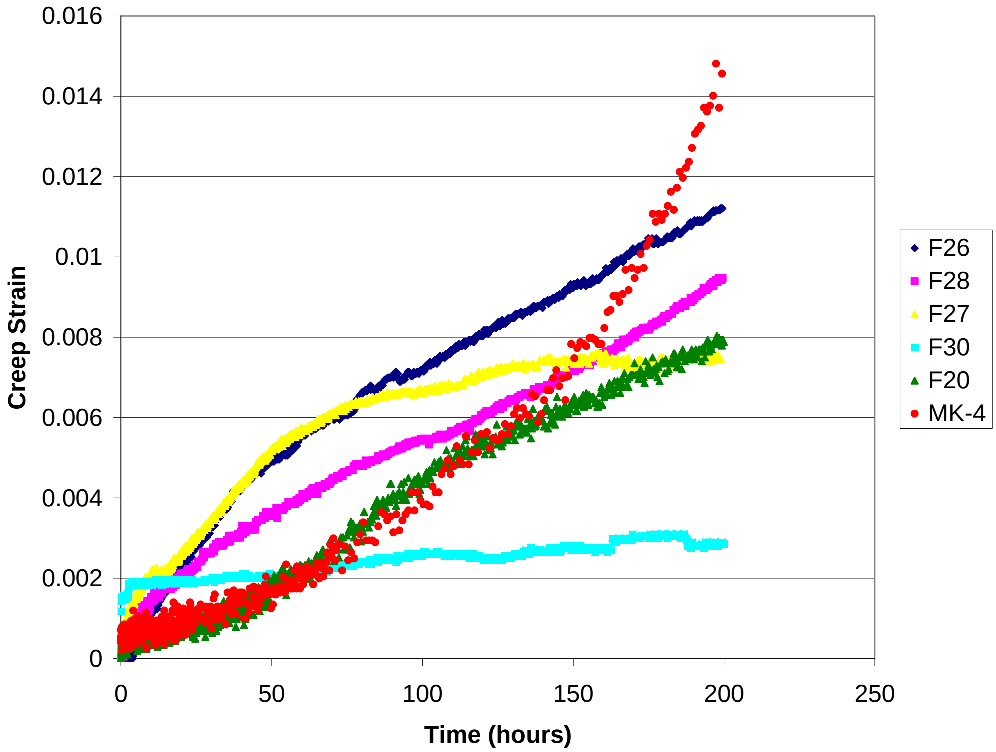


Figure 7 - Creep Behavior at 950°C and 290 MPa for 200 Hours

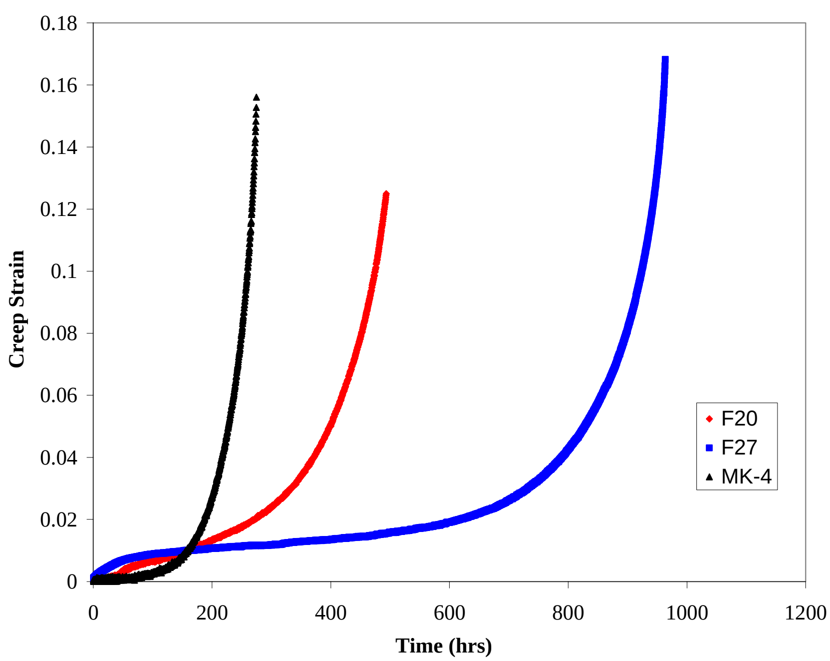


Figure 8 – Creep Rupture Behavior at 950°C and 290 MPa

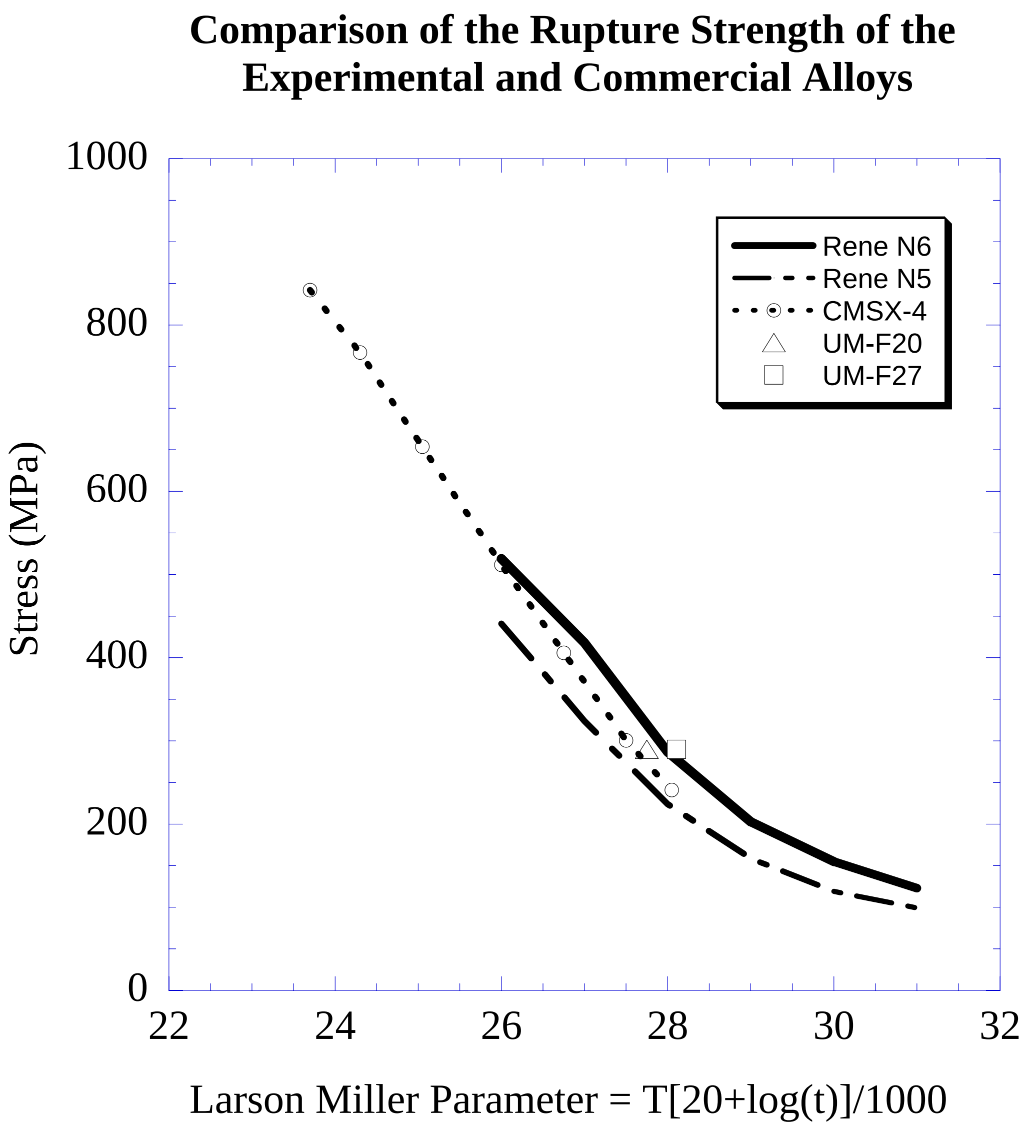


Figure 9 – Laron-Miller plot for commercial superalloys compared to experimental superalloys.